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Growth and characterization of antimony thiourea bromide (ATB)

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Abstract Single crystals of the metal organic nonlinear optical material, antimony thiourea bromide (ATB) were grown from sodium meta silicate gel at ambient temperature. The conditions for the growth of large ATB single crystals of dimension 10 mm × 5 mm × 5 mm in gel were obtained. X-ray analysis confirmed the crystal structure to be orthorhombic with space group $Cmc2_1$. The grown crystals were characterized by EDAX, FTIR, TGA, DSC and Microhardness studies. Spectroscopic studies on ATB reveal the presence of sulphur-to-antimony bonds in the complex. Thermal analysis indicates that the material melts at 96°C.

Keywords Antimony thiourea bromide (ATB) , gel growth ; FTIR analysis

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1. Introduction

Performance requirements of nonlinear optical devices have placed severe demand on the materials used in those devices. For several years, many workers have carried out an intense search for new materials and a wide variety of both organic and inorganic materials have been developed. Problems with both classes of materials have resulted in the investigation of semiorganics [1-4]. The materials have the potential for combining the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics. The approach of combining the high nonlinear optical coefficients of organic molecules with the excellent physical properties of the inorganics, has been found to be overwhelmingly successful in the past. Thiourea, which is otherwise centrosymmetric, yields excellent noncentrosymmetric materials and typifies this approach [5]. Based on the intuitive approach to introduce the asymmetric conjugated organic molecules into an inorganic distorted polyhedra, several thiourea complexes were synthesized and screened for their powder efficiencies and ATB was identified as one of the promising candidates. ATB belongs to the orthorhombic crystal class with the space group $Cmc2_1$. ATB is noncentrosymmetric and exhibits NLO properties.

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2. Experiment

ATB crystals are grown using single diffusion technique from gel. Due to gel medium properties, gel growth allows one to obtain nearly defect-free crystals useful in optical applications. The gel is a two-phase medium formed by a three dimensional polymer network containing growth solution. The gel structure consequently suppresses large-scale movements i.e. convection currents, which can disrupt crystal perfection. In addition, the probability of nucleation is largely reduced by the presence of a condensed gel phase which, during growth, is rigid enough to support the crystal, but is still compatible with the crystal development. Crystal growth then mainly takes place in the diffusion regime [6].

Sodium meta silicate (SMS) solution of density 1.04 g/cc is acidified with acetic acid and mixed with thiourea solution (inner reactant). The time for gelation is varied from 12 to 24 hours. Antimony trioxide dissolved in HBr is added as the outer reactant which diffuses into the gel medium and the reaction takes place according to the following equation

$$Sb_2O_3 + CS(NH_2)_2 + HBr \rightarrow Sb[CS(NH_2)_2]Br_3 . \quad (1)$$

The gel density, pH and the concentration of the reactants are varied and the optimum conditions for the growth of good single crystals are found to be 1.04 g/cc, pH 5, 1M Sb_2O_3 and 1M thiourea.

3. Characterization

The grown crystals have been subjected to powder X-ray diffraction to confirm the structure. Energy dispersive analysis by X-rays (EDAX) has been taken to confirm the elements present in the crystal. Fourier transform infra red (FTIR) spectra of ATB and thiourea are recorded to reveal the metal complex coordination. Simultaneous Thermogravimetric analysis – Differential thermogravimetry (TGA-DTG) and Differential scanning calorimetry (DSC) analyses have been carried out to determine the thermal stability and the phase transition involved in the grown crystal. Powder X-ray diffraction has been recorded by crushing the crystal into fine powder for ATB single crystal. Fourier transform IR spectra of ATB is recorded in the range 400 – 4000 cm^{-1} employing spectrometer in the form of solids dispersed in KBr pellets. DTG/TGA is carried out using PERKIN – ELMER 7 Series thermal analysis system between 50 and 1000°C. Similarly, the DSC analysis of the crystal has been performed on Netzsch – Geratebau GmbH thermal analysis system between 0 and 250°C. Microhardness is determined using Shimadzu HMV 2000 Vickers hardness tester.

4. Results and discussion

X-ray powder diffraction pattern was obtained for ATB crystal. The sample is scanned over the range 10 – 50° at a rate of 5°/min. The lattice parameters are found to be a = 12.39 (2) Å, b = 11.68 (3) Å, c = 18.64 (1) Å and the cell volume V = 2698.71 $Å^3$ and these values agree well with the reported one [7]. The present and the reported values of cell parameters are given in Table 1 and the observed and calculated d values are given in Table 2.

The elements present in the crystal are confirmed by EDAX analysis. This analysis also confirms the absence of impurities such as sodium, silicon in the crystal. Figure 1 shows the EDAX

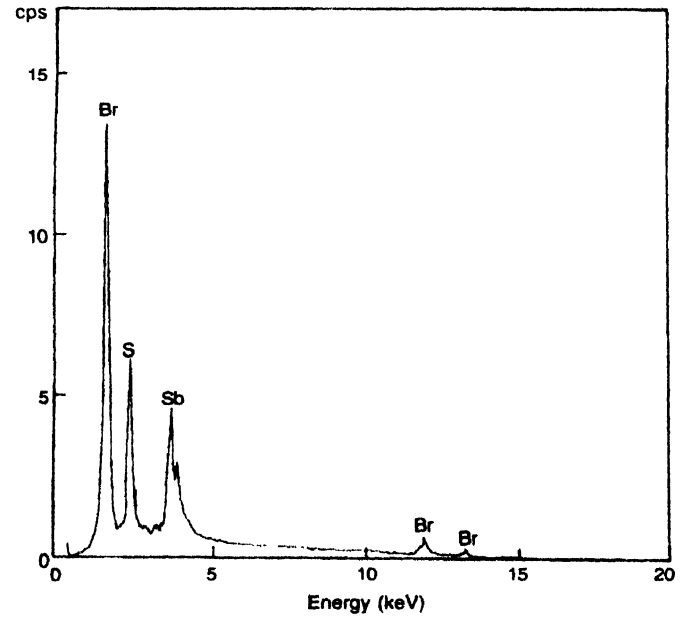


Figure 1. EDAX analysis of ATB.

Table 1. Cell parameters (present and reported values)

present values	reported values
a = 12.39 (2) Å	a = 12.272 (3) Å
b = 11.68 (3) Å	b = 11.675 (4) Å
c = 18.64 (1) Å	c = 18.617 (5) Å

Table 2. Powder X-ray diffraction data for ATB single crystal.

Experimental d values (Å)	Calculated d values (Å)	hkl
7.7517	7.7344	111
6.2766	6.2808	112
5.0221	5.0164	113
4.2604	4.2561	023
4.0916	4.0865	114
3.7155	3.7152	130
3.6435	3.6435	131
3.5011	3.4951	124
3.2868	3.2971	230
3.1899	3.1887	133
3.0769	3.0814	215
2.9785	2.9883	034
2.9224	2.9207	040
2.9057	2.9050	134
2.7841	2.7871	042
2.6866	2.6916	234
2.6405	2.6419	240
2.5405	2.5413	117
2.5007	2.5011	325
2.4748	2.4749	044
2.4239	2.4244	430
2.3854	2.3848	340
2.2780	2.2789	151
2.2545	2.2559	335
2.1941	2.1937	406
2.1644	2.1644	137
2.1541	2.1538	153
2.1409	2.1417	523
2.0897	2.0900	327
2.0662	2.0653	600
2.0499	2.0491	524
2.0153	2.0164	602
1.9734	1.9740	138
1.9287	1.9284	129
1.9024	1.9029	238
1.8618	1.8619	229
1.8491	1.8484	261
1.8197	1.8209	119

curve for ATB single crystals. The peaks corresponding to the presence of antimony, sulphur and bromine at different energies are shown. The IR spectra of ATB crystal is recorded in Testscan Shimadzu FTIR 8000 series spectrophotometer in the range 400-4000 cm^{-1} in the form of solids dispersed in KBr powder (Figure 2). Crystal structure investigation of thiourea has

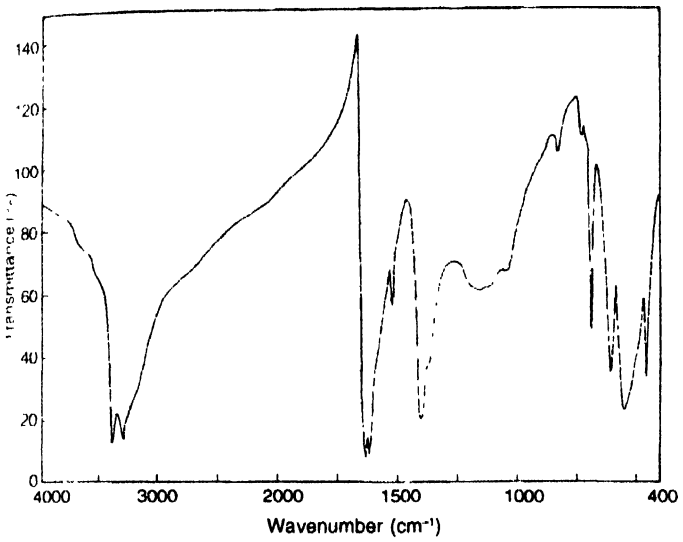
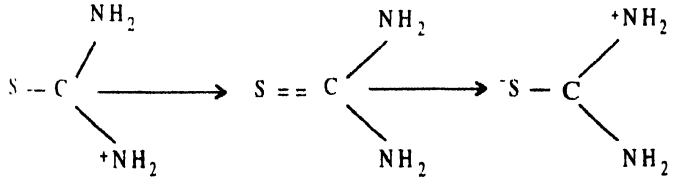


Figure 2. FT-IR spectrum of ATB

established the coplanarity structure of C, N and S atoms in the molecule [4]. The electronic structure of thiourea may be represented by a resonance hybrid of structures I, II and III as shown below.



I II III

The effect of metal coordination complexes of thiourea vibrations has been less extensively studied. The study of the spectra of thiourea [8] and bismuth thiourea chloride (BTC) shows a shift in the frequency band in the low frequency range. Most of the metals form complexes with sulphur [9]. The structure of ATB reveals that Sb bonds with S. On complex formation with different types of ligands, the metal-sulphur peak is expected to lie in the lower wavelength region [10]. The absorption at 455.2 cm^{-1} crystal corresponds to 469 cm^{-1} of thiourea which can be assigned to symmetric C = S stretching. The absorption at 607.5 cm^{-1} for ATB corresponds to 630 cm^{-1} of thiourea. This can be attributed to asymmetric N-C-N bending vibration. The absorption at 686.6 cm^{-1} corresponds to 720 cm^{-1} of thiourea. The lowering of frequency can be attributed to the reduced double bond character of C = S bond on coordination. The absorption at 1043.4 cm^{-1} corresponds to 1010 cm^{-1} of thiourea, which is due to NH_2 vibration. The absorptions at 1122.5 cm^{-1} and 1404.1 cm^{-1} match with the 1090 cm^{-1} and 1390 cm^{-1} absorption of thiourea and can be assigned to symmetric CN stretching. The absorption at 1631.7 cm^{-1} corresponds to 1625 cm^{-1} of thiourea and this can be assigned to NH_2 bending. The absorptions at 3280.7 cm^{-1} and 3377.1 cm^{-1} match with 3295 cm^{-1} and 3385 cm^{-1} of thiourea which is due to asymmetric NH_2 stretching. A comparison of vibrations of thiourea with ATB crystal is shown in table 3, confirms the metal – sulphur bonding of ATB.

Table 3. Assignment of FTIR peaks

Thiourea	ATB cm^{-1}	Assignment
469	455.2	δ_s (NCS)
630	607.5	δ_{as} (NCS)
720	686.6	γ_s (CS)
1010	1043.4	τ (NH_2)
1090	1122.5	γ_s (CN)
1390	1404.1	γ (CN)
1625	1631.7	δ (NH_2)
3295	3280.7	γ_{as} (NH_2)
3385	3377.1	γ_{as} (NH_2)

δ – bending vibration; τ – non planar vibration; γ – stretching; s – symmetric; s – symmetric; as – asymmetric

The DTG/TGA curve of ATB shown in Figure 3 illustrates the decomposition at different stages with maximum weight loss at 332°C.

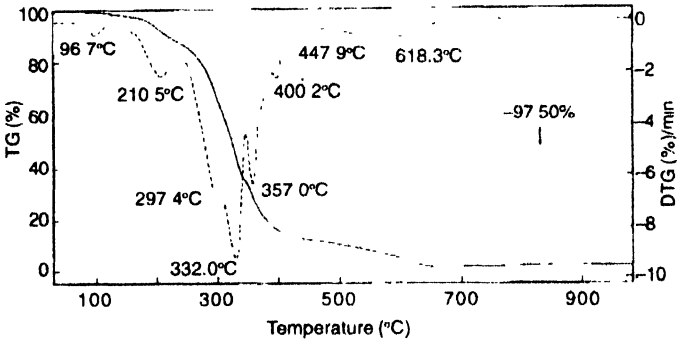


Figure 3. DTG/TGA of ATB.

The DSC trace shown in Figure 4 shows an exothermic peak at 101.3° C and three endothermic peaks at 114.4°C, 198.2°C and 208.7°C. The peak at 101.3°C is sharp and it is suspected to be due to melting. In order to confirm this, the sample has been separately tested for its melting point using Hot Stage Optical Microscope. The compound is observed to start melting at 96°C

supporting our presumption. This coincides with the weight loss observed in TGA.

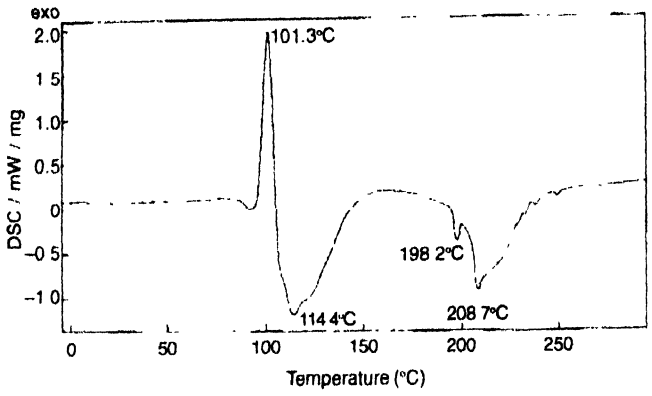


Figure 4. DSC of ATB

The hardness of ATB is carried out using Vicker's pyramidal indenter. Indentations are made for various loads from 5 to 100 g. Several tests are carried out for different loads, and the average value of the diagonal length of the indentation mark corresponding to each load is used for estimating the microhardness. The variation of microhardness with indenter load is shown in Figure 5. The hardness increases with the applied load and attains a constant. At lower loads, the hardness is less and when the load is increased, the hardness increases and attains a constant value. The hardness is found to increase with increase of load from 5g to 15 g and thereafter almost remains constant upto 100g. Berzina *et al* [11] have explained the increase of microhardness with increase of load for alkali halide crystals, considering the effect of surface layer of crystals on the value of microhardness. According to them, during indentation, the impression of the diamond pyramid may penetrate to a depth comparable with, or considerably greater than, the thickness of the surface layer. Even at smaller loads the surface layer of the crystal is pierced by the indenter and so it shows a marked effect for all small loads. As the depth of indentation increases, the effect of surface layer becomes less and for larger loads, when the impression reaches a depth at which an undistorted layer of material exists, the value of microhardness becomes independent of load.

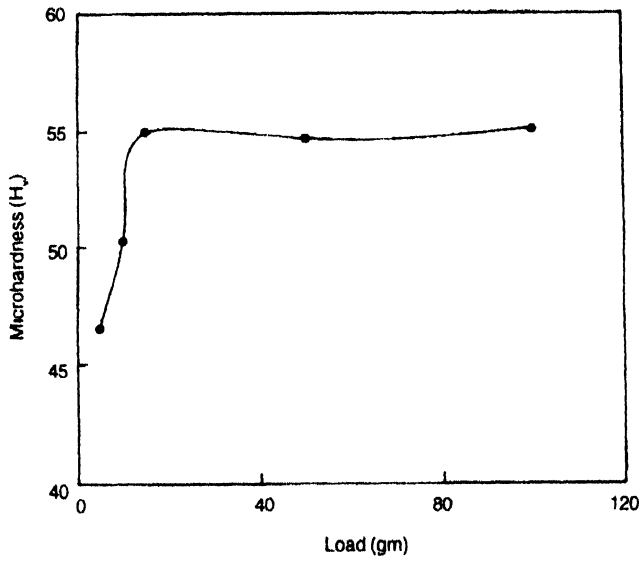


Figure 5. Hardness *vs* indenter load plot of ATB.

5. Conclusions

Antimony thiourea bromide crystals (ATB) were grown by gel technique. The powder XRD pattern was recorded and indexed for use in the characterization during subsequent syntheses. ATB was found to crystallize in the orthorhombic system with space group $Cmc2_1$. It is noncentrosymmetric and exhibits NLO property. Thermal analyses showed that the melting point of the compound is indeed 101.3°C. Spectroscopic investigation revealed that there is a shift in the frequency band in the low frequency region which reveals that thiourea forms sulphur to antimony bonds in the ATB crystal. The hardness test showed that it increases with the indenter load and attains a constant value. The Vicker's hardness number (H_v) is found to be 55 Kg/mm^2.

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References

[1] N Zhang, M Jiang, D Yuan, D Xu and X Tao *Chinese Phys. Lett.* **6** 280 (1989)

[2] N Zhang, M H Jiang, D R Yuan, D Xu, X T Tao and Z S Shao *J. Cryst. Growth* **102** 581 (1990)

[3] J T Lin, W S Wang and H Arend *SPIE Proc.* **1104** 100 (1989)

[4] G D Andreetti, L Cavalca and A Musatti *Acta Cryst.* **B24** 683 (1968)

[5] V Venkatramanan, S Maheswaran, J N Sherwood and H L Bhat *J. Cryst. Growth* **179** 605 (1997)

[6] P Andreazza, D Josse, F Lefaucheux, M C Robert and J Zyss *Phys. Rev.* **B45** 7640 (1992)

[7] S G Bhat and S M Dharmaprakash *J. Cryst. Growth* **181** 390 (1997)

[8] B Ya Shteinberg, Yu I Mushkin and A I Finkelshtein *Opt. Spectrosc.* **33** (1972) 589

[9] K Swaminathan and H M N H Irving *J. Inorg. Nucl. Chem.* **26** 1291 (1964)

[10] K Nakamoto *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn. (New York : Wiley - Interscience) p 343 (1978)

[11] E G Berzina, I B Berman and P A Sanitsev *Sov. Phys. Crystallography* **9** 483 (1965)